Quantum Chemical Study of Mechanisms for Oxidative Dehydrogenation of Propane on Vanadium Oxide

Scientific Achievement

A hybrid density functional study of mechanisms for oxidative dehydrogenation of propane on the (010) surface of V_2O_5 and on vanadia clusters on a TiO_2 substrate has been carried out. A Mars-van Krevelen mechanism was investigated that involves stepwise adsorption of the propane at an oxygen site followed by desorption of a water molecule and subsequent adsorption of an oxygen molecule to complete the catalytic cycle. The potential energy surface for the (010) surface is found to have large barriers, which are lowered somewhat when the possibility of a triplet state is considered. Nevertheless, the highest energy on the potential energy surface at the B3LYP/6-31G(*) level of theory is about 80 kcal/mol above the energy of the reactants and corresponds to formation of an oxygen vacancy after water elimination. Subsequent addition of an oxygen molecule to fill the vacancy is predicted to be energetically downhill. The barriers for propane adsorption and propene elimination are also large (50-60 kcal/mol). Investigation of a similar reaction mechanism for V_2O_x dimers on a TiO_2 substrate is found to have significantly lower barriers when the dimer is hydroxylated and are in agreement with experiment. The hydroxylation causes the dimer to be in a reduced state and is more reactive. (P. Redfern, P. Zapol, M. Sternberg, S. Zygmunt, S. Adiga, and L. Curtiss, *J. Phys. Chem. B*, in press).

Significance

Obtaining a molecular understanding of catalysis is a key to being able to control the selectivity and activity of new catalysts, which is important for reducing energy requirements in the industry. This computational study represents the first step in obtaining a molecular level understanding of the effect of substrates in activating catalytic clusters for oxidative selective catalytic reactions. The results suggest experiments should be done to determine whether the vanadia clusters have hydroxyl groups on them to establish the oxidation state of the cluster. In future work, theory will be used to examine the dependence of catalytic activity on cluster size, type of substrate, and the structure of the substrate. This is part of a combined experimental/theoretical project on catalytic nanoporous membranes, which has been initiated in the Materials Science Division in collaboration with Northwestern University and the Chemistry Division.

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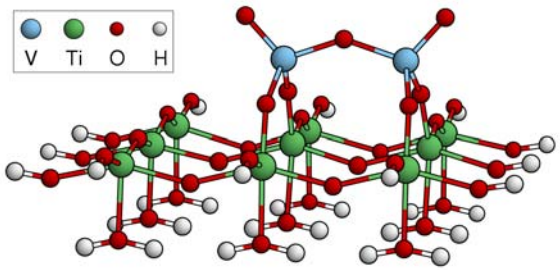
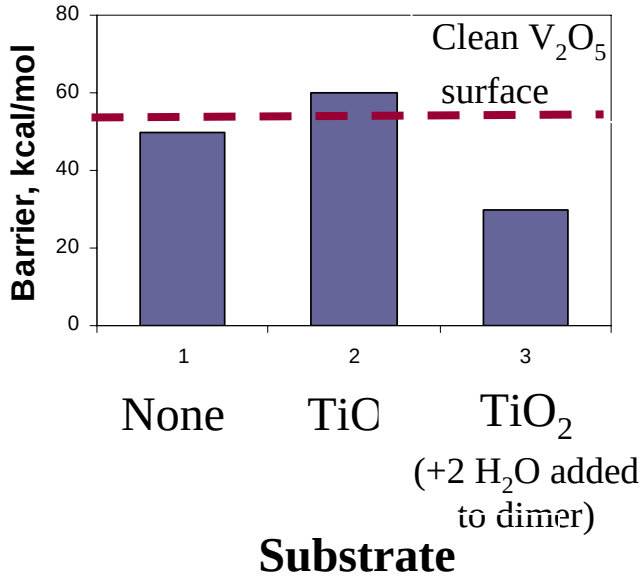


Vanadia cluster on TiO_2 substrate



- Hydroxylated dimer on TiO_2 substrate is in agreement with experiment
- Results indicate a dramatic difference in reactivity of VOx dimer for propane dehydrogenation depending on its oxidation state.
- First step in obtaining a molecular level understanding of oxidative selective catalytic reactions in catalytic nanoporous membranes through combined experimental/theoretical studies

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